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Quantification of excitation-power dependency in Tm^{3+}/Yb^{3+} doped fluorotellurite upconverting glass phosphor for iris recognition

Bingrui Li[a], Xin Zhao[a], Edwin Yue Bun Pun[b], Hai Lin[a,b,*]

[a] School of Information Science and Engineering, Dalian Polytechnic University, Dalian 116034, China
[b] Department of Electronic Engineering and State Key Laboratory of Millimeter Waves, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

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ABSTRACT

Excitation-power dependency of upconversion (UC) photons have been quantified in Tm^{3+}/Yb^{3+} doped fluorotellurite (BALMT) glasses under the excitation of 975 nm laser. The net powers of three-photon-excited blue and red and two-photon-excited NIR emissions are determined to be 242, 101 and 7994 μW in 0.5 wt% Tm_2O_3 and 2 wt% Yb_2O_3 co-doping case under the excitation power of 870 mW, respectively, and the net emission photon numbers are identified to be 58.2×10^{13}, 33.0×10^{13} and 3253.2×10^{13}cps. The quantum yields (QYs) for multi-photon-excited UC emissions of Tm^{3+} are identified as a positive dependency with pumping powers, and the relativity for three-photon fluorescence is extremely severe. When the excitation power density is set to 110.8 W/mm^2, the QY values for 476 nm blue and 650 nm red UC emissions are up to 1.49×10^{-4} and 0.84×10^{-4}, and furthermore, the value for 809 nm NIR UC emission is as high as 83.22×10^{-4}. The 809 nm luminescence is one of the good matching wavelengths for iris recognition in NIR ranges, the intensive NIR luminescence and the efficient blue fluorescence are promising in scanning and positioning for iris scanning. The macroscopic quantization for UC photon generation from Tm^{3+} in low-phonon fluorotellurite glasses provides a reliable reference for developing compact high-power-density light sources in iris recognition.

1. Introduction

High-brightness near-infrared (NIR) light source is widely used in medical treatment, infrared radar, remote sensing, iris recognition and other fields, especially in iris recognition it acquires increasing attention owing to the bioactivity, the non-lesion and the high penetration [1–3]. In iris scans, the larger-power white light beam will make people narrow their eyes leading to the incompleteness of image, which seriously may burn the human eyes. And meanwhile, the eye image gained with the visible light is not clear enough to be accurately identified by the device. Fortunately, near-infrared light obtained via secondary low-energy photon absorption in upconversion (UC) mechanism can get iris features with clear diagrams and avoid the damage to eye cells [4–8]. Simultaneously, quantitative evaluation for UC photons of rare-earth (RE) ions gives an intuitive reference for the advancement and improvement on optical properties of high-density illumination devices. Therefore, the study on high-quality UC irradiation light source without signal interfering compared with the visible one is in great demand [9–17].

In order to achieve powerful UC emissions, tellurite glasses have been attempted and they are proved to be good hosts due to the lower phonon energy and the higher RE solubility [18–22]. Based on tellurite glasses, the addition of fluorine ions could modify the local ligand field of RE^{3+} ions in a glass host matrix [23–28]. Meanwhile, the introduction of fluorine ions can release hydrogen spices and reduce the OH^- presence, leading a macro upgrade for the fluorescent intensity of the radiative emissions in RE^{3+} ions [29–38]. Inasmuch as the emission quantum efficiency from a given level depends strongly on the phonon energy of the host medium, it can be expected that the fluorescence quantum efficiency strengthened obviously with the inlet of fluorine ions [39–46]. Hence, it is of significance to give considerable interest for RE^{3+}-ion-doped fluorotellurite glass systems. Among them, Tm^{3+} has gained increasing attention because its meta-stable levels are suitable for emitting blue, red and near-infrared UC luminescence [47–55]. Moreover, quantitative characterization on Tm^{3+}-doped glasses will be beneficial to securing an excellent NIR luminescence that can be used as light source for iris scans.

The schematic diagram of iris recognition system adopting glass phosphor as the irradiative light source is demonstrated in Fig. 1, and the efficient NIR luminescence and blue fluorescence are promising in

* Corresponding author at: School of Information Science and Engineering, Dalian Polytechnic University, Dalian 116034, China.
E-mail address: lhai@dlpu.edu.cn (H. Lin).

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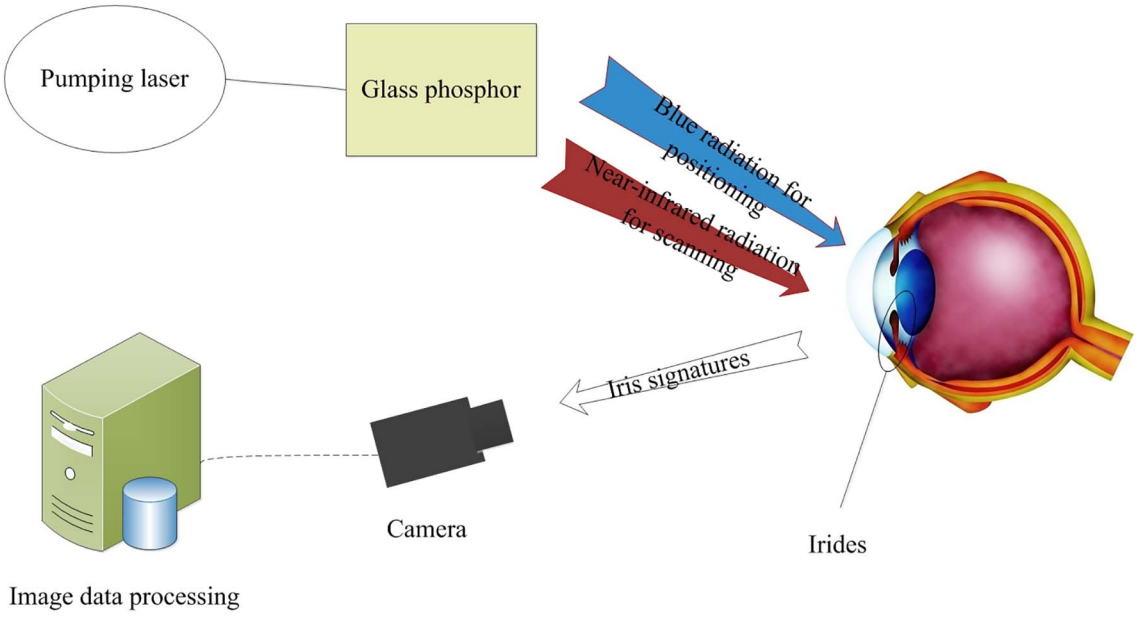

Fig. 1. Schematic diagram of iris recognition system adopting a glass phosphor as the irradiation light source.

scanning and positioning for this system. In this work, Tm^{3+}/Yb^{3+} co-doped fluorotellurite glass phosphors have been prepared and characterized. Efficient three-photon-excited blue and intense two-photon-excited NIR upconversion fluorescence was observed and recorded under the excitation of 975 nm laser at room temperature. The quantum yields (QYs) of 476 nm blue and 809 nm NIR UC emissions are as high as 1.49×10^{-4} and 83.22×10^{-4} when the excitation power density is 110.8 W/mm^2. The best matching ranges for iris recognition are 700–900 nm in the NIR ranges. Among them, 809 nm NIR fluorescence shows an excellent recognition performance, the texture quality score, the false rejection rate and the equal error rate of 809 nm are 85%, 0.0327 and 0.00617, respectively. So the 809 nm NIR luminescence from Tm^{3+}/Yb^{3+} doped fluorotellurite glass is one of the good matching wavelengths for iris recognition. High texture quality and prominent recognition performance of 809 nm manifest that the Tm^{3+}/Yb^{3+} co-doped fluorotellurite glass is in favor of achieving an excellent NIR luminescence that can be used as light source for iris recognition.

2. Materials and methods

RE^{3+} ions doped BALMT glasses were prepared from high-purity BaF_2, AlF_3, La_2O_3, MgO and TeO_2 powders according to the molar host composition $4BaF_2–4AlF_3–6La_2O_3–16MgO–70TeO_2$ (BALMT). Additional 0.5 wt% Tm_2O_3 and 1 wt% Yb_2O_3, and 0.5 wt% Tm_2O_3 and 2 wt% Yb_2O_3 were added based on the host weights. The well-mixed raw materials were first melted in a platinum crucible at 850 °C for 15 min using an electric furnace, and subsequently followed by quenching on an aluminum plate. All the samples were annealed at 340 °C for 2 h and cooled down to room temperature inside the furnace to relax the inner stress, and then sliced and polished with two parallel sides for optical measurements.

The density of 0.5 wt% Tm_2O_3 and 1 wt% Yb_2O_3 co-doped glass was measured to be 5.42 g·cm^{-3}, thus the number density of Tm^{3+} ions is 8.335×10^{19}cm^{-3}. Using the Metricon 2010 prism coupler, the refractive indices of the 0.5 wt% Tm_2O_3 and 1 wt% Yb_2O_3 co-doped glass were measured to be 1.9931 and 1.9471 at 635.96 nm and 1546.9 nm, respectively. The refractive indices at all other wavelengths can be given by Cauchy's equation $n = A + B/\lambda^2$ [56] with A = 1.9377 and B = 22,389 nm^2. The absorption spectrum was recorded with a Perkin Elmer UV-VIS-NIR Lambda 750 spectrophotometer. Visible fluorescence spectra were determined by a Hitachi F-7000 fluorescence spectrophotometer adopting a 975 nm laser as the pumping source.

The spectral power distribution of glass samples was determined in an integrating sphere with 3.3-inch diameter, which was connected to a QE65000 CCD detector (Ocean Optics) and a USB4000 CCD detector (Ocean Optics) with a 600 μm core optical fiber, and a fiber pigtailed 975 nm multimode diode laser was adopted as the excitation source. A standard halogen lamp (Labsphere, SCL-050) was used to calibrate this measurement system, and spectral power distribution of the lamp was acquired through fitting the factory data based on the blackbody radiation law. All the above measurements were carried out at room temperature and the luminescence photographs of the samples were taken by an iPad mini 2.

3. Results

In order to objectively demonstrate the multi-photon excitation mechanism of the UC emission fluorescence, fluorescence spectrophotometer adopting a 975 nm pumping laser was used to record the luminescence from the sample surface, and the emission spectra of 0.5 wt% Tm_2O_3 and 2 wt% Yb_2O_3 co-doped BALMT glass were shown in Fig. 2. In each spectrum, there are three emission peaks, which located at 793, 650 and 480 nm and corresponding to the $^3H_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ transitions, respectively. For the three luminescence peaks, the dependence of up-conversion emission intensities on excitation powers was derived and presented in Fig. 3. The fitted function of the log-log plots is $y = a + bx$, where y is the fluorescence intensity, a is a constant, b is the fitted slope, x is the pumping power. And the b for the 793, 650 and 480 nm emissions are 1.84, 2.54 and 2.61, confirming that the $^3H_4$, $^1G_4$ and $^1G_4$ emitting states are populated predominantly by two-, three- and three-photon absorption processes, respectively.

When pumped by a 975 nm laser diode, Tm^{3+} ions cannot utilize the excitation energy directly owing to the lack of matched energy level, but Yb^{3+} can absorb the NIR radiation efficiently and transfer the excitation energy to Tm^{3+} via three possible energy transfer (ET) processes as shown schematically in Fig. 4. First Tm^{3+} ions are excited to the $^3H_5$ level by ET from Yb^{3+} and partly relax to the $^3F_4$ level. Subsequently, some of them arrive at the $^3F_{2,3}$ levels through ET and excited state absorption (ESA) and then relax to the lower meta-stable state $^3H_4$. The Tm^{3+} at the $^3H_4$ level relaxes radiatively to the ground state $^3H_6$ producing the two-photon-excited NIR emission. Finally, a